

# PATENT SPECIFICATION (11)

1 358 520

1 358 520

(21) Application No. 26097/72 (22) Filed 5 June 1972

(44) Complete Specification published 3 July 1974

(51) International Classification C07C 63/26

(52) Index at acceptance

C2C 220 227 22Y 265 26Y 297 30Y 24X 366 367 37X 409  
46Y 490 638 668 69Y BQ

(19)



## (54) OXIDATION OF AROMATIC ORGANIC COMPOUNDS

SPECIFICATION NO 1358520

By a direction given under Section 17 (1) of the Patents Act 1949 this application proceeded in the name of INSTITUT FRANCAIS du PETROLE, a Body Corporate organised and existing under the laws of France, of 1 & 4 Avenue de Bois-Preau, 92 502 Rueil-Malmaison, Hauts-de-Seine, France.

R 77195/4

THE PATENT OFFICE

BEST AVAILABLE COPY

15 which it is to be performed, to be particularly described in and by the following statement:—

This invention concerns a process for the liquid-phase oxidation of aromatic organic compounds to produce polycarboxylic aromatic acids.

20 A crucial problem faced by industry in the liquid phase oxidation of aromatic organic compounds, particularly xylenes to phthalic acids, is the efficient removal of the heat of reaction from the oxidation zone.

25 The invention aims to provide a process in which dissipation of the heat of reaction and dehydration of solvent may be achieved in a simple, economical, efficient and commercially feasible manner.

30 The invention provides a process for producing a polycarboxylic aromatic acid which comprises reacting an aromatic organic compound having at least two oxidizable aliphatic side chains with an oxygen-containing gas in the presence of an oxidation catalyst and an inert reaction diluent in a primary oxidation zone, while maintaining a liquid phase in the said zone, to obtain a conversion of at least 90% in the said zone; passing the reaction off-gases from the said oxidation zone to a distillation zone prior to any appreciable condensation of the off-gases, recycling at least a portion of the bottoms of the said distillation zone to the said oxidation zone, the said bottoms containing from 1 to 10% by weight of water; conducting the overhead vapour from the distillation zone to a condensation zone, separating effluent from the condensation zone into a

off-gases from the oxidation vessel to the bottom portion of the distillation column, a condenser, transfer means for conducting overhead vapours from the distillation column, a condenser, transfer means for separating non-condensable gases from the condensate, transfer means for conducting condensate from the condenser to the separating means, transfer means for returning condensate to the distillation column and transfer means for returning non-condensable gases from the separating means to the oxidation vessel.

75 Examples of aromatic organic compounds which may be oxidized by the process of this invention are xylenes, for example *para*-xylene, and other alkyl-substituted aromatic hydrocarbons. Some other suitable feedstocks are described in U.S. Patents Nos. 2,245,528 (Loder), 2,276,774 (Henke) and 3,387,027 (Alagy).

80 The oxygen-containing gas may consist of substantially 100% pure oxygen gas or it may be in the form of a gaseous mixture containing lower concentrations of oxygen, for example air. It is preferred to use air because it is the least expensive of the suitable oxygen-containing gases. A suitable ratio of oxygen to the aromatic compound 90 is 3.5 to 7.5 moles, preferably 4 to 6 moles, of oxygen per mole of aromatic compound.

95 Well known oxidation catalysts suitable for use in the process of this invention are metals or compounds of metals which are selected from the heavy metal group as defined in the periodic chart of elements on pages 56 and 57 of the *Handbook of Chem-*

(21) Application No. 26097/72 (22) Filed 5 June 1972

(44) Complete Specification published 3 July 1974

(51) International Classification C07C 63/26

(52) Index at acceptance

C2C 220 227 22Y 265 26Y 297 30Y 34X 366 367 37X 409  
46Y 490 638 668 69Y BQ

(19)



## (54) OXIDATION OF AROMATIC ORGANIC COMPOUNDS

(71) I, KEITH JOHN ALLEN CRAMPTON, of British Nationality, of D. Young & Co., of 9 & 10 Staple Inn, London, W.C.1, do hereby declare the invention, which has been communicated to me from abroad by INSTITUTE FRANCAIS DU PETROLE DES CARBURANTS ET LUBRIFIANTS, a body corporate organised and existing under the laws of France, of 1 & 4 avenue de Bois-Préau, 92 502 Rueil-Malmaison, Hauts-de-Seine, France, and for which I pray that a patent may be granted to me, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention concerns a process for the liquid-phase oxidation of aromatic organic compounds to produce polycarboxylic aromatic acids.

A crucial problem faced by industry in the liquid phase oxidation of aromatic organic compounds, particularly xylenes to phthalic acids, is the efficient removal of the heat of reaction from the oxidation zone.

The invention aims to provide a process in which dissipation of the heat of reaction and dehydration of solvent may be achieved in a simple, economical, efficient and commercially feasible manner.

The invention provides a process for producing a polycarboxylic aromatic acid which comprises reacting an aromatic organic compound having at least two oxidizable aliphatic side chains with an oxygen-containing gas in the presence of an oxidation catalyst and an inert reaction diluent in a primary oxidation zone, while maintaining a liquid phase in the said zone, to obtain a conversion of at least 90% in the said zone; passing the reaction off-gases from the said oxidation zone to a distillation zone prior to any appreciable condensation of the off-gases, recycling at least a portion of the bottoms of the said distillation zone to the said oxidation zone, the said bottoms containing from 1 to 10% by weight of water; conducting the overhead vapour from the distillation zone to a condensation zone, separating effluent from the condensation zone into a

liquid stream and a vapour stream containing non-condensable gas, and introducing non-condensable gas, during at least a portion of the period during which oxygen is being substantially completely consumed, into the oxidation zone in an amount sufficient to cause a decrease in the temperature of the oxidation zone of about 5 Centigrade degrees.

The process may be carried out in apparatus comprising an oxidation vessel, a distillation column, transfer means for conducting off-gases from the oxidation vessel to the bottom portion of the distillation column, a condenser, transfer means for conducting overhead vapours from the distillation column, a condenser, transfer means for separating non-condensable gases from the condensate, transfer means for conducting condensate from the condenser to the separating means, transfer means for returning condensate to the distillation column and transfer means for returning non-condensable gases from the separating means to the oxidation vessel.

Examples of aromatic organic compounds which may be oxidized by the process of this invention are xylenes, for example *para*-xylene, and other alkyl-substituted aromatic hydrocarbons. Some other suitable feedstocks are described in U.S. Patents Nos. 2,245,528 (Loder), 2,276,774 (Henke) and 3,387,027 (Alagy).

The oxygen-containing gas may consist of substantially 100% pure oxygen gas or it may be in the form of a gaseous mixture containing lower concentrations of oxygen, for example air. It is preferred to use air because it is the least expensive of the suitable oxygen-containing gases. A suitable ratio of oxygen to the aromatic compound is 3.5 to 7.5 moles, preferably 4 to 6 moles, of oxygen per mole of aromatic compound.

Well known oxidation catalysts suitable for use in the process of this invention are metals or compounds of metals which are selected from the heavy metal group as defined in the periodic chart of elements on pages 56 and 57 of the *Handbook of Chem-*

istry, 8th Edition, Handbook Publishers, Inc., Sandusky, Ohio, 1952. Such metals include cobalt, manganese, iron, nickel, lead, tin, molybdenum, tungsten, cerium and neodymium. Other catalysts which are suitable are described in the above-mentioned U.S. Patents.

In addition to the catalysts, conventional initiators such as ketones, aldehydes, and bromine-containing compounds may be used if desired.

The reaction diluent is usually a monocarboxylic acid that is relatively inert to the oxidation conditions used in the process of this invention and preferably contains from 1 to 8 carbon atoms per molecule. Saturated aliphatic acids which contain 2 to 4 carbon atoms per molecule and are free of hydrogen atoms attached to tertiary carbon atoms are particularly preferred, acetic acid being particularly preferred.

The amount of acid used as reaction diluent can be 0.1 to 30 parts per part of aromatic material by weight. The acid is preferably used in amounts from 0.5 to 20, especially from 1 to 10 parts per part of aromatic compound.

The temperature at which the oxidation is effected is generally between 100 and 220°C. It is preferably between 120 and 180°C, especially between 140 and 170°C.

The pressure at which the oxidation is effected is usually between 3 and 25 atmospheres, preferably between 4 and 10 atmospheres.

The residence time in the oxidation vessel is generally between 0.5 and 10 hours, preferably between 1 and 5 hours.

The various reaction parameters are selected so that at least 90%, preferably at least 96%, conversion is attained in the said oxidation zone. Preferably the parameters are selected so that a yield of at least about 95% is attained in the entire process.

If a conversion of less than 90% were obtained in the said oxidation zone, it would be necessary to use at least one subsequent oxidation zone in order to obtain a worthwhile product yield. Large quantities of heat would be generated in the subsequent oxidation zone due to the high degree of conversion occurring therein and consequently a crucial heat removal problem would result.

However, if, in the process of the invention, a subsequent oxidation zone is employed, the heat of reaction generated in the said subsequent oxidation zone is quite small and can be easily dissipated by merely adding cold acetic acid to the subsequent oxidation zone or even employing a jacketed vessel.

In a preferred embodiment of the process of the present invention, the reaction product from the primary oxidation zone is

conducted to at least one subsequent independently operated oxidation zone.

When at least two oxidation zones are used, the subsequent oxidation zone should be operated at a higher temperature and/or higher oxygen partial pressure than the primary oxidation zone. Such operating conditions are necessary in the subsequent oxidation zone(s) in order to reduce the quantity of oxidation intermediates such as *para*-toluic acid and *para*-carboxybenzaldehyde produced by converting them to terephthalic acid.

It is preferred to transfer the reaction product from the primary oxidation zone to a subsequent oxidation zone without the utilization of a pump. This can be achieved by using in the subsequent zone an oxidizing gas, such as pure O<sub>2</sub>, having a much higher oxygen content than that in the primary zone (e.g. about 10 times as great). Accordingly, the total pressure in the subsequent oxidation zone can be lower while the oxygen partial pressure can be higher than that in the primary oxidation zone. Therefore, the higher pressure in the primary oxidation zone (e.g. about 7 atmospheres) can be used to force the reaction product to the subsequent oxidation zone at the lower pressure (e.g. about 6 atmospheres).

Attempts to operate the primary oxidation zone to obtain complete conversion along with acceptable yields would not be completely successful. The amounts of impurities produced including tar-like oxidation products would be increased due to use of increased temperatures or the residence time in the reactor would be too long to be feasible for an industrial operation. Accordingly, the yield of the preferred oxidized product, e.g. terephthalic acid, would be decreased. Also these tar-like oxidation products would tend to coat the surfaces of the desired product rendering its recovery and purification quite difficult.

When the oxidation is effected in two stages, a product of higher purity can be obtained in greater yield: raw material losses and total reaction volume are lower than when the oxidation is effected in a single stage.

In such a process, the primary oxidation zone is usually at a temperature of between 140°C and 170°C, and at a pressure between 4 and 10 atmospheres and the reaction residence time in the primary oxidation zone should be between about 1 and about 5 hours.

The oxygen partial pressure at the gas-liquid interface in the primary oxidation zone is usually between 0.1 and 2 atmospheres and preferably between 0.2 and 1 atmospheres.

The subsequent oxidation zone is usually at a temperature of between 150°C and

180°C, preferably about 175°C, and at a pressure between 4 and 50 atmospheres, preferably between 6 and 7 atmospheres. The reaction residence time in the subsequent oxidation zone should be between about 0.5 and about 2 hours.

The oxygen partial pressure in the dispersed gas phase of the second oxidation zone is usually between 2 and 50 atmospheres. The partial pressure of the oxygen when pure oxygen is used would be somewhat less than the reactor pressure. This is so because, as the temperature increases, the pressure of the diluent increases, vaporizing the diluent into the rising oxygen bubbles. Preferably the subsequent oxidation zone is operated with no overhead vapour space. Of course, more than two oxidation zones can be used if desired.

The process of this invention can be carried out either continuously, batchwise, or intermittently. It is preferred, however, that the reaction be a continuous one because of the economics involved. Higher product purity may also be obtained in continuous process as compared to batch or intermittent processes.

Conducting the off-gases from the oxidation zone to the distillation zone prior to any appreciable condensation of the vapours, not only dissipates the heat of reaction by vapourization of the diluent such as acetic acid, but also provides the thermal energy required for the distillation. This eliminates the necessity and cost of employing a reboiler and supplying heat or energy to the reboiler as would be required if condensation of the off-gases occurred prior to distillation.

It has also been found that the fractionation system of the present invention is inherently stable. The oxidation reaction produces more than enough heat with which to control the water content of the oxidation vessel at any through put or air addition rate, since the heat of reaction automatically fluctuates with the water production in the oxidation reaction and hence with the amount of water to be removed.

Another advantage of the process of this invention is that, since the condenser is placed after the distillation column, it can be up to about 50% smaller in size than if it were placed before the distillation column since improved heat transfer occurs in the present case. This is due to the fact that the composition is changed from one containing predominantly acetic acid and air to one containing predominantly water and air with resultant improvements in the film coefficient.

Also, in the process of the invention, it is not necessary to use a cooler to condense the off-gas from the condenser since this off-gas does not contain such large quantities of

solvent vapour, (e.g. acetic acid), as would be present if the condenser was located before the distillation column. In addition, if a condenser and a condensate accumulator were present it would be necessary to have a distillation column and distillate accumulator. The present process eliminates the need for a second conductor and accumulator.

The bottoms which are removed from the distillation column should contain from 1 to 10% by weight of water. This amount of water is needed to guarantee a very efficient oxidation process. Amounts greater than 10% will reduce the reaction rate and amounts less than 1% will have a similar effect. The best results are obtained when about 3 to 7% by weight of water is present in the bottoms which are to be recycled to the oxidation zone.

It is useful but not essential to introduce non-condensable gas into the liquid phase of the primary oxidation zone.

Preferably the non-condensable gas which is introduced into the liquid phase of the oxidation zone is the dehydrated gas obtained at the top of the distillation column. Generally, the gas is obtained from an accumulator placed after the distillation column to insure adequate dehydration of the gas. Such gas obviously does not affect the explosive or non-explosive nature of the vapor phase leaving the oxidation zone.

It is, of course, understood that non-condensable gases obtained from other sources can be used. Examples of such gases are mixtures of carbon monoxide or carbon dioxide and oxygen, air or nitrogen.

The advantage of recycling gas is more associated with "steady state" continuous operation than with start-up or batch operations where the recycling of inert gas is practiced in order to avoid explosions. In the steady state case the introduction of the gas permits operations to be effected over a wider range of temperatures and pressures than would be characteristic of an operation without recycle gas; it is possible to effect the oxidation using a higher pressure and/or a lower temperature than when such a gas is not introduced. For instance, if it were found necessary to increase the pressure and no gas were added, not only would the pressure increase but so would the temperature.

The reason why it is preferred to effect the oxidation at increased pressure is that it has been found that higher oxygen partial pressures help to prevent accumulation of oxidation inhibitors in the recycle acetic acid which ultimately result in gross inhibition of the reaction. If the temperature is permitted to increase along with the increase in pressure, the quantity of tar-like oxidation products also increases. These in turn not

only decrease the yield of the preferred oxidized product, such as terephthalic acid, but also coat the particles of acid thereby rendering the recovery and purification of the acid product more difficult.

Accordingly, it can be seen that the introduction of the non-condensable gas is advantageous. For instance, the rate of reaction at a particular temperature can be increased by the introduction of the gas along with an increase in the pressure and the maintenance of the temperature at the same level.

On the other hand if it is desired to improve the product by reducing tar-like oxidation products, the pressure can be kept the same while the introduction of the gas provides for a decrease in the temperature of the reaction. This will be accompanied by a corresponding increase in the oxygen partial pressure due to the lower vapor pressure of the diluent.

Of course, it is important not to decrease the temperature to too low a level, since the rate of reaction decreases as the temperature decreases. In addition it is possible both to decrease the temperature and increase pressure according to the amount of gas added.

In order for the introduction of the non-condensable gas to produce a noticeable affect on either the type of product or the rate of reaction, it must be added in an amount sufficient to decrease the temperature by at least 5°C while keeping the pressure constant. Due to the introduction of the non-condensable gas into the liquid phase, the amount of diluent, for example acetic acid, that vaporizes is increased. This is due to the fact that the gas leaving the oxidation zone tends to be saturated with the acetic acid, and, accordingly, if more gas is present then more acetic acid can vaporize. As a consequence of the additional acetic acid vaporization, more heat of reaction is dissipated which in turn reduces the temperature of the reaction. Also, when the non-condensable gas is used in conjunction with an increase in the pressure, it is most advantageous to increase the pressure by at least  $\frac{1}{2}$  atmosphere. Less than a  $\frac{1}{2}$  atmosphere increase with a constant temperature will not noticeably increase the conversion of recycle intermediates.

The point of introduction of the gas into the liquid phase is a compromise between the degree of reduction in the average partial pressure of the oxygen which can be tolerated and the amount of contact between the diluent and the gas which is desired. If the gas is introduced into the liquid phase at too low a level in the oxidation zone, the average partial pressure of the oxygen is reduced. If it is substantially reduced the rate of reaction is adversely affected.

On the other hand, if the gas is introduced

at a point too close to the top of the liquid phase, the contact time between the diluent and the gas may not be sufficient to achieve liquid vapor equilibrium. The gas is then not as effective or efficient in reducing the temperature of the oxidation zone. The particular point of introduction of the gas should therefore be chosen based on which of these advantages or disadvantages is of greatest concern. It is found desirable that the gas be introduced into the top half of the liquid phase, and preferably into the top 25% of the liquid phase, e.g. at a part between the upper 25% and the upper 1% of the liquid phase. Very suitable results have been obtained by introducing the gas at a point about 10% down from the top of the liquid phase.

Also it has been found that the presence of a scrubbing means between the primary oxidation zone and the distillation zone, although not essential, may be advantageous. The scrubbing means reduces the quantities of corrosive materials entering the distillation zone. The reduction of corrosive materials however, is not sufficient to permit the use of materials other than corrosion resistant materials in the construction of the distillation zone.

An example of apparatus in which the process of the present invention can be carried out is described below with reference to the single figure of the accompanying drawings.

A primary oxidation vessel 4 is provided with material inlet lines 1 and 3, product outlet line 5 and a vapour stream outlet line 6. A line 2 joins line 1 before line 1 enters oxidation vessel 4. Vapour outlet line 6 connects to the bottom portion of a scrubber 7, which has an overhead vapour outlet line 9, and a bottoms outlet line 8. Bottoms outlet line 8 connects to the upper portion of oxidation vessel 4, while overhead vapour line 9 leads to the bottom portion of a distillation column 10. Distillation column 10 is provided with a bottoms outlet line 12, an intermediate outlet line 11 and an overhead vapour outlet line 15. Bottoms product line 12 splits up into lines 13 and 14. Line 13 leads to the top of scrubber 7 while line 14 leads to oxidation vessel 4. Overhead vapour outlet line 15 connects to a condenser 16 which has an outlet line 17. Outlet line 17 of condenser 16 leads to accumulator 18 which is provided with a liquid stream outlet line 19 and a vapour stream outlet line 22. Outlet line 19 splits up into lines 20 and 21, with line 20 connecting to the upper portion of the distillation column 10. Overhead vapour line 22 is provided with a valve 23 and leads to line 24.

Product outlet line 5 from the primary oxidation vessel 4 connects to a subsequent oxidation vessel 25. The subsequent oxida-

tion vessel 25 is provided with additional material inlets 26 and 27, product outlet line 28, and overhead vapour outlet line 29.

For convenience, the operation of the apparatus is described with respect to the oxidation of *para*-xylene in an acetic acid solution employing cobalt acetate as catalyst, hydrogen bromide as promoter, and air as the oxygen-containing gas.

The *para*-xylene, cobalt acetate, hydrogen bromide promoter and acetic acid are introduced into oxidation vessel 4 through lines 2 and 1, the *para*-xylene being added to the other ingredients via line 1. The air is introduced at the bottom portion of the oxidation vessel 4 by means of line 3. The reaction product is removed as the bottoms from the oxidation vessel 4 through line 5. The overhead vapor, which contains nitrogen, oxygen, acetic acid, water, *para*-xylene, entrained liquid droplets and entrained solid particles leaves oxidation vessel 4 and is introduced into the scrubber 7 through line 6. In scrubber 7 the vapor stream is contacted with a liquid stream flowing counter-currently in order to remove entrained solid particles.

The treated vapour stream leaves scrubber 7 through line 9 and enters distillation column 10 as the feed at the bottom. The liquid stream is removed from scrubber 7 through line 8 and is introduced into the upper portion of oxidation vessel 4.

A bottoms liquid stream composed of mostly *para*-xylene, acetic acid and from about 1 to 10% water is removed from distillation column 10 through line 12. A portion of this liquid stream is introduced into scrubber 7 through line 13 and is employed as the scrubbing liquid therein. The remaining portion of the liquid stream is introduced into the oxidation vessel 4 through line 14. Either or both of these streams may be cooled between distillation column 10 and reactor 4 and/or scrubber 7. An intermediate liquid stream may be removed from distillation column 10 through line 11 for use as a washing stream for later purification operations.

An overhead vapor stream which contains predominantly nitrogen, oxygen, and water vapor passes through line 15 to condenser 16. In condenser 16 a substantial amount of the water is condensed. An effluent is removed from condenser 16 through line 17.

The effluent from condenser 16 which contains both condensate and vapor is conducted via line 17 to accumulator 18. A liquid stream which contains predominantly water is removed from the accumulator through line 19 and a vapor stream containing non-condensable gases is removed from the accumulator through line 22. A portion of the liquid stream is returned to distillation column 10 through line 20 as reflux

while the remainder of the liquid stream is taken off through line 21 and sent to a suitable waste water treating facility (not shown). The waste water stream from line 21 contains small amounts of acetic acid. The overhead vapour stream is passed through lines 22 and 31 to valve 23 and through line 24 to a suitable scrubber (not shown) for removing any remaining traces of acetic acid from the gases prior to venting them to the atmosphere. Valve 23 can be adjusted so as to regulate the system pressure. It is also possible to pass a portion of the overhead vapour through line 30 back to line 14 wherein it is mixed with the bottoms from distillation column 10 and is then fed to oxidation vessel 4.

The reaction product from the primary oxidation vessel 4 is fed to the subsequent oxidation vessel 25 through line 5. Additional cobalt acetate, hydrogen bromide promoter, and acetic acid can be introduced into oxidation vessel 25 through line 27. The air is introduced at the bottom portion of the oxidation vessel by means of line 26. The overhead vapour leaves oxidation vessel 25 through line 29 and the product is removed as the bottoms from the oxidation vessel through line 28.

The following Example, in which all parts are by weight unless the contrary is set forth, is given to further illustrate the invention.

#### EXAMPLE 1

One part of 99.5% pure *para*-xylene, 10 parts/hour of acetic acid, 0.1 parts/hour of cobalt bromide are fed into a glass-lined steel primary oxidation vessel. Air is introduced at the bottom of the reaction vessel at an average flow rate of about 8 parts/hour. The temperature of the oxidation vessel is maintained between about 148°C and about 150°C, and the pressure is between about 5 and about 5.2 atmospheres. A vapor stream is removed from the oxidation vessel and is fed to a scrubber. In the scrubber the vapor stream is treated by contact with a liquid stream flowing counter-currently to it. The vapor stream leaving the scrubber is substantially free of any corrosive metals and is then fed to a distillation column. The liquid stream leaving the scrubber is sent to the liquid phase of the oxidation vessel.

Some of the distillation column bottoms is used for scrubber liquid feed and the rest is returned to the oxidation reactor. An intermediate stream containing about 90 parts water and about 10 parts acetic acid is removed from the distillation column and can be utilized in subsequent purification treatments of the terephthalic acid product. An overhead vapor stream containing about 13 parts nitrogen, about 1 part oxygen and water vapor is removed from the distillation column and is fed to a condenser where-



in substantially all of the water vapor is condensed to liquid water. About 0.3 parts of the condensate is removed from the system and the remaining part is recycled to the distillation column as reflux. The retention time in the primary oxidation vessel is about 2 hours.

The product from the primary oxidation vessel is conducted into a glass-lined steel subsequent oxidation vessel. Oxygen is introduced at the bottom of this vessel at an average flow rate of about 0.1 part/hour. The temperature in this oxidation vessel is maintained between about 170°C and about 175°C, and the pressure is between about 4.5 and about 4.7 atm. The retention time in the subsequent oxidation vessel is about 1 hour. 1.55 parts of a terephthalic acid product of 99.5% purity are removed from this vessel as the product.

#### WHAT WE CLAIM IS:—

1. A process for producing a polycarboxylic aromatic acid which comprises reacting an aromatic organic compound having at least two oxidizable aliphatic side chains with an oxygen-containing gas in the presence of an oxidation catalyst and an inert reaction diluent in a primary oxidation zone, while maintaining a liquid phase in the said zone, to obtain a conversion of at least 90% in the said zone, passing the reaction off-gases from the said oxidation zone to a distillation zone prior to any appreciable condensation of the off-gases, recycling at least a portion of the bottoms of the said distillation zone to the said oxidation zone, the said bottoms containing from 1 to 10% by weight of water; conducting the overhead vapour from the distillation zone to a condensation zone, separating effluent from the condensation zone into a liquid stream and a vapour stream containing non-condensable gas, and introducing non-condensable gas, during at least a portion of the period during which oxygen is being substantially completely consumed, into the oxidation zone in an amount sufficient to cause a decrease in the temperature of the oxidation zone of about 5 Centigrade degrees.

2. A process according to claim 1, in which the aromatic organic compound is *para*-xylene.

3. A process according to claim 1 or 2, in which the oxygen-containing gas is air.

4. A process according to claim 1, 2 or 3, in which the oxidation catalyst is cobalt bromide.

5. A process according to any preceding claim, in which the inert reaction diluent is a C<sub>1-8</sub> monocarboxylic acid.

6. A process according to claim 5, in which the inert reaction diluent is acetic acid.

7. A process according to any preceding claim, in which the overhead vapour from the distillation zone is conducted to a condensation zone, effluent from the condensation zone is separated into a liquid stream and a vapour stream containing non-condensable gas and at least a portion of the said vapour stream is employed as the said non-condensable gas.

8. A process according to any preceding claim, in which the non-condensable gas is introduced into the liquid phase at a point which is between the upper 25% and the upper 1% of the liquid phase.

9. A process according to any preceding claim, in which the reaction product from the oxidation zone is conducted to at least one subsequent oxidation zone which is operated at a higher temperature and/or a higher oxygen partial pressure than the primary oxidation zone.

10. A process according to claim 9, in which the subsequent oxidation zone(s) is/are operated with no overhead vapour space.

11. A process according to claim 9, in which the reaction product from the primary oxidation zone is conducted to the subsequent oxidation zone(s) by the total pressure drop between the primary and the subsequent oxidation zone(s).

12. A process according to claim 9, 10 or 11, in which pure oxygen is used as oxidizing gases in the subsequent oxidation zone(s).

13. A process according to any preceding claim, carried out in apparatus comprising an oxidation vessel, a distillation column, transfer means for conducting off-gases from the oxidation vessel to the bottom portion of the distillation column, a condenser, transfer means for conducting overhead vapour from the distillation column to the condenser, means for separating non-condensable gases from the condensate, transfer means for conducting condensate from the condenser to the separating means, transfer means for returning condensate to the distillation column and transfer means for returning non-condensable gases from the separating means to the oxidation vessel.

14. A process according to claim 13, in which the apparatus also comprises a scrubbing means interposed between the oxidation vessel and the distillation column, a transfer means for conducting the off-gases from the oxidation vessel to the bottom portion of the scrubbing means and a transfer means for conducting the liquid bottoms from the distillation column to the upper portion of the scrubbing means.

15. A process according to claim 1, carried out in apparatus substantially as hereinbefore described with reference to the accompanying drawing.

16. A process according to claim 1, sub-

stantially as hereinbefore described in the  
Example.

17. Polycarboxylic aromatic acids, when  
prepared by a process according to any one  
5 of the preceding claims.

For the Applicants,  
D. YOUNG & CO.,  
Chartered Patent Agents,  
9 and 10 Staple Inn,  
London, WC1V 7RD.

Printed for Her Majesty's Stationery Office by Burgess & Son (Abingdon), Ltd.—1974.  
Published at The Patent Office, 25 Southampton Buildings, London, WC2A 1AY,  
from which copies may be obtained.

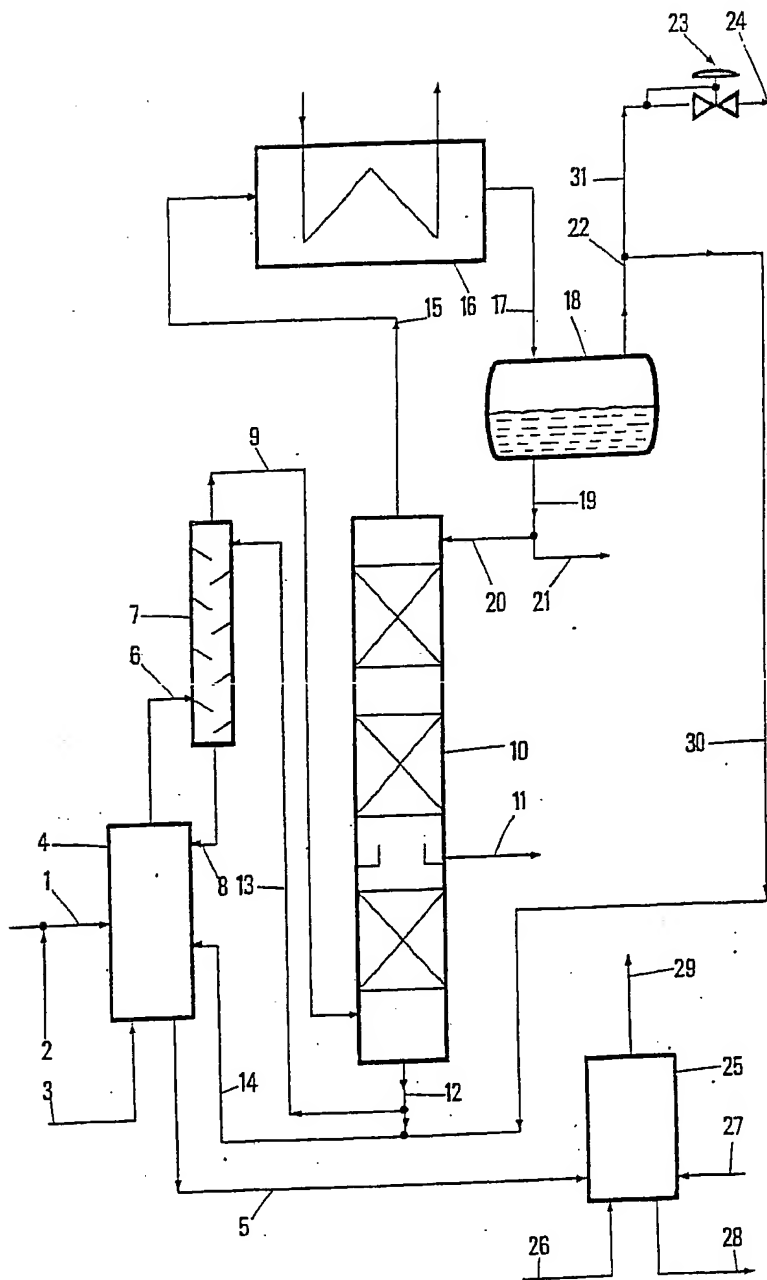


1358520

## COMPLETE SPECIFICATION

1 SHEET

*This drawing is a reproduction of  
the Original on a reduced scale*



**This Page is Inserted by IFW Indexing and Scanning  
Operations and is not part of the Official Record**

**BEST AVAILABLE IMAGES**

Defective images within this document are accurate representations of the original documents submitted by the applicant.

Defects in the images include but are not limited to the items checked:

- ☐ BLACK BORDERS
- ☐ IMAGE CUT OFF AT TOP, BOTTOM OR SIDES
- ☒ FADED TEXT OR DRAWING
- ☒ BLURRED OR ILLEGIBLE TEXT OR DRAWING
- ☐ SKEWED/SLANTED IMAGES
- ☐ COLOR OR BLACK AND WHITE PHOTOGRAPHS
- ☐ GRAY SCALE DOCUMENTS
- ☒ LINES OR MARKS ON ORIGINAL DOCUMENT
- ☒ REFERENCE(S) OR EXHIBIT(S) SUBMITTED ARE POOR QUALITY
- ☐ OTHER: \_\_\_\_\_

**IMAGES ARE BEST AVAILABLE COPY.**

**As rescanning these documents will not correct the image problems checked, please do not report these problems to the IFW Image Problem Mailbox.**